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VACUUM MEASUREMENTS BY

TIME-OF-FLIGHT MASS SPECTROMETRY



F. G. Sherrell and A. J. Mathews

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FOREWORD

The work reported herein was sponsored by Arnold Engineering Development Center (AEDC), Air Force Systems Command (AFSC), under Program Element 65402234.

The results of research presented were obtained by ARO, Inc. (a subsidiary of Sverdrup & Parcel and Associates, Inc.), contract operator of the AEDC, AFSC, Arnold Air Force Station, Tennessee, under Contract AF40(600)-1200. This work was performed in the Aerospace Environmental Facility (AEF), under ARO Project No. SW3411, from May 1, 1965, through May 6, 1966. The manuscript was submitted for publication on July 18, 1966.

The instruments used during this work were commercial instruments that were not necessarily designed or manufactured either to meet Government specifications or to operate as applied during this activity. Any difficulty encountered during the application of these instruments to the problem investigated herein is no reflection on the instruments or any manufacturer.

The assistance of C. A. Neal, who did the computer programming of the data reduction problems, is greatly appreciated.

This technical report has been reviewed and is approved.

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ABSTRACT

Procedures are discussed for using mass spectrometers to make absolute partial pressure measurements of complicated residual gas mixtures in high vacuum systems. The details of the matrix inversion technique and an iteration procedure for calculating partial pressures from mass spectrometer data are presented. Performance of a Bendix Model 17-210V time-of-flight mass spectrometer and calibration data obtained are given. These data indicate that short-term instrument stability cannot be assumed for mass spectrometers which use electron multipliers for ion detection, and that instrument linearity can be assumed only under certain operating conditions. The data show that frequent, in-place, mass spectrometer calibrations are necessary. The matrix inversion technique and the iteration procedure were evaluated experimentally by reducing the 17-210V spectrum of a 12-component mixture of common residual gases whose partial pressures were known. The experimental results indicate that the iteration technique is the simplest to apply, and that it produces more accurate partial pressure solutions. It is concluded that accuracies of ± 15 percent in partial pressure measurements are obtainable.

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SECTION I INTRODUCTION

The most informative way to specify the vacuum which exists in a space simulator is in terms of the absolute partial pressures of the residual gases. Measurements of absolute partial pressures can be made by using a mass spectrometer which has been calibrated against absolute partial pressure standards. Standard partial pressures for calibration can readily be established (Ref. 1). When the mixture of residual gases consists only of components such as hydrogen, helium, water vapor, and the components of air, partial pressure measurements are simple and yield satisfactory results. However, mixtures which include these gases and high concentrations of hydrocarbon gases are often encountered. The absolute partial pressure analysis of this type of mixture is more difficult because the various components usually interfere in the mass spectrum. That is, several components in the mixture usually give rise to ion current at the same mass numbers.

Analysis of such a mixture is made as follows: (1) The types of residual gases assumed to be present in the vacuum system are determined by any means possible, such as consideration of qualitative mass spectrometer data, vacuum system design information, and data on outgassing of materials. This determination must include all gases which are present to a significant degree in the vacuum system. (2) The mass spectrometer is then calibrated in terms of the absolute partial pressure of each type of gas. (3) The mass spectrum of the residual gas mixture under study is recorded. (4) The resulting spectrum is reduced to obtain the absolute partial pressure of each type of residual gas.

The objectives of this project are to establish procedures for the routine accomplishment of steps (2), (3), and (4) above. A vacuum calibration system was developed previously in the project for use during mass spectrometer calibrations (step 2). A description of this system, which was used throughout the present work, is presented in Ref. 1. A commercial, Bendix Model 17-210V, time-of-flight mass spectrometer was chosen for use in establishing these procedures. Calibration data on the 17-210V are presented for a specific set of instrument operating parameters. Although these calibration data are valid only for the 17-210V, the data reduction techniques presented are applicable to data taken with any of the various other types of mass spectrometers (partial pressure analyzers) which are capable of unit mass resolution over the range of interest.

SECTION II
THEORY OF PARTIAL PRESSURE ANALYSIS

A mass spectrometer operates on the principle that if one pure gas is present in the ion source, then the ion current, H_ℓ , which is generated at atomic mass number ℓ is directly proportional to the partial pressure, p , of the gas:

$$h_\ell p = H_\ell \quad 1 \leq \ell \leq m \quad (1)$$

The proportionality constant, h_ℓ , is the sensitivity factor at mass number ℓ , and m is the largest mass number in the spectrum of the pure gas. The set of H_ℓ values is the cracking pattern of the pure gas.

A second basic feature of mass spectrometer operation is that if there is a mixture of n residual gases in the ion source then the spectra of the n components add linearly according to the set of equations (Ref. 2):

$$\begin{aligned} h_{11}p_1 + h_{12}p_2 + \cdots + h_{1n}p_n &= H_1 \\ h_{21}p_1 + h_{22}p_2 + \cdots + h_{2n}p_n &= H_2 \\ \vdots &\quad \vdots & \vdots & \vdots \\ \vdots &\quad \vdots & \vdots & \vdots \\ \vdots &\quad \vdots & \vdots & \vdots \\ h_{m1}p_1 + h_{m2}p_2 + \cdots + h_{mn}p_n &= H_m \end{aligned} \quad (2)$$

In general, the number of equations in the set exceeds the number of unknowns. The set of constants, H_ℓ , in Eq. (2) is the mass spectrum of the unknown mixture of gases, and m is the largest mass number in the spectrum. The factor h_{mn} is the spectrometer sensitivity for gas n at mass number m . The other sensitivity factors are defined in a similar manner.

The sensitivity factors are determined experimentally by calibrating the mass spectrometer against a standard partial pressure of each pure gas. During this calibration, Eq. (1) is used to calculate the sensitivity factor for each gas at each mass number. These factors are then substituted into Eq. (2). For example, Fig. 1 shows the equations which describe the mass spectrum of a specific 12-component mixture. The coefficients are in units of amp/torr and constitute the calibration of the Bendix 17-210V time-of-flight mass spectrometer for the 12 gases. The superscript on the coefficients is to be interpreted as an exponent of ten. The partial pressure of each type of gas is identified on the figure. For example, the first term in the second equation is read 4.65×10^{-4} (amp/torr) times the partial pressure of hydrogen. The subscript on the constants, H_ℓ , is in atomic mass units, and the major peak in the

cracking pattern of each pure gas is underlined. A successful partial pressure analysis requires solving such a set of equations to obtain an accurate set of solutions.

2.1 MATRIX INVERSION TECHNIQUE

The conventional way of solving a set of equations like that of Fig. 1 is to employ the methods of matrix algebra (Refs. 2 and 3). In doing so a subset of n equations is chosen from Eq. (2). The number of equations selected, and consequently the number of ion current peaks which are actually used during the data reduction, corresponds to the number of unknown partial pressures.

These equations may be written in the form:

$$\begin{aligned} h_{11}p_1 + h_{12}p_2 + \dots + h_{1n}p_n &= H_1 \\ h_{21}p_1 + h_{22}p_2 + \dots + h_{2n}p_n &= H_2 \\ &\vdots && \vdots \\ &\vdots && \vdots \\ &\vdots && \vdots \\ h_{n1}p_1 + h_{n2}p_2 + \dots + h_{nn}p_n &= H_n \end{aligned} \quad (3)$$

The subscript on the constant terms in Eq. (3) denotes the equation number rather than the atomic mass number. However, each of the n equations applies to a specific mass number. By defining the coefficient matrix, h , to be the square matrix

$$h = \begin{pmatrix} h_{11} & h_{12} & \dots & h_{1n} \\ h_{21} & h_{22} & \dots & h_{2n} \\ \vdots & \vdots & & \vdots \\ \vdots & \vdots & & \vdots \\ \vdots & \vdots & & \vdots \\ h_{n1} & h_{n2} & \dots & h_{nn} \end{pmatrix} \quad (4)$$

and by further defining p and H vectors as

$$p = \begin{pmatrix} p_1 \\ p_2 \\ \vdots \\ p_n \end{pmatrix} \quad H = \begin{pmatrix} H_1 \\ H_2 \\ \vdots \\ H_n \end{pmatrix} \quad (5), (6)$$

Equation (3), expressed in the terms of matrix algebra, becomes

$$hp = H \quad (7)$$

Multiplying both sides of Eq. (7) by h^{-1} gives (Refs. 2 and 3)

$$p = h^{-1}H \quad (8)$$

Thus, data reduction by the matrix inversion technique involves three steps: (1) choosing a subset of n equations from Eq. (2), (2) calculating the h^{-1} of the subset, and (3) carrying out the matrix multiplication indicated by Eq. (8).

This first step is discussed in the following section, and procedures for calculating h^{-1} are outlined in the Appendix.

2.1.1 Choice of Equations

The matrix inversion technique may produce inaccurate solutions if the subset of n equations selected from Eq. (2) is ill-conditioned (Ref. 4). The difficulty encountered when attempting to solve a system of ill-conditioned equations is that small measurement and round-off errors in the coefficients, Eq. (4), generate large errors in the solutions. Out of the complete set of m equations it is possible to choose N different subsets of n equations where $N = [m! / n! (m - n)!]$. The degree of ill-conditioning of these N possible choices will vary from one subset to the next, and the use of an ill-conditioned subset should be avoided. A convenient measure of ill-conditioning is presented by Stanton (Ref. 4). In this measure, the n linear equations, Eq. (3), are considered to represent n hyperplanes in n -dimensional space, and the angle of intersection of the i and j planes is given by

$$\cos^2 \theta_{ij} = \frac{\left[\sum_{k=1}^n h_{ik} h_{jk} \right]^2}{\sum_{k=1}^n h_{ik}^2 \sum_{k=1}^n h_{jk}^2} \quad (9)$$

The i and j specify two of the equations in Eq. (3), and the h_{ik} and h_{jk} are the corresponding coefficients in these equations. In applying Eq. (9) it is convenient to let i vary successively from $1 \leq i \leq (n - 1)$, and for each value of i , to let j vary successively from $(i + 1) \leq j \leq n$. This procedure generates a total of $[n! / 2(n - 2)!]$ values of $\cos^2 \theta_{ij}$. If any of these values are near unity, then the corresponding angles are small and the equations are ill-conditioned.

This measure of ill-conditioning can be employed while choosing a subset of n equations from Eq. (2). In this procedure the $[m! / 2(m - 2)!]$ values of $\cos^2 \theta_{ij}$ are calculated on the computer from Eq. (9), and those values exceeding 0.1, say, are tabulated. The n rows, Eq. (3), are then chosen as follows: The equations corresponding to the major peaks (i.e., the largest h) of the n unknowns are noted. This choice is made initially because the accuracy of the measurements of these peaks is usually better than that of the minor peaks. If one of these equations contains the major peak of more than one unknown, then the equation or equations containing the next largest sensitivity factors of those particular unknowns are noted. By using this procedure a preliminary choice of n equations is made. Using the tabulated $\cos^2 \theta_{ij}$ values, the equations corresponding to the larger $\cos^2 \theta_{ij}$ values are noted; if one equation is involved more often than the others, it is deleted and a substitute made. The new set is then checked, and other substitutions made to further reduce the ill-conditioning. This procedure is clarified by an example in section IV.

Inevitably, some arbitrary decisions are involved in this procedure. However, the measure of ill-conditioning, Eq. (9), does at least provide a means of avoiding the use of one of the more ill-conditioned subsets. The objective of this procedure is to choose a subset of n equations which:

- (1) Includes all n unknowns,
- (2) Has the smallest $\cos^2 \theta_{ij}$ terms possible, and
- (3) Includes the major peak, or at least one prominent peak, in the spectrum of each gas.

In general, these last two requirements conflict, and the final choice will represent an arbitrary compromise. Since the final choice may still be somewhat ill-conditioned, considerations of the errors in partial pressure solutions are necessary.

2.1.2 Errors in Partial Pressure Solutions

Partial pressure solutions obtained by the matrix inversion technique may be in error as a result of small measurement errors in either the coefficients or the constant terms of Eq. (3). The magnitudes of the errors in the solutions will depend both on the magnitudes of the measurement errors and on the degree of ill-conditioning of the n chosen equations. The following expression of the uncertainties in a set of partial pressure solutions of Eqs. (3) or (8) is easily derived (Ref. 5):

$$\begin{aligned}
 h_{11}\Delta p_1 + h_{12}\Delta p_2 + \cdots + h_{1n}\Delta p_n &= \Delta H_1 - (p_1\Delta h_{11} + p_2\Delta h_{12} + \cdots + p_n\Delta h_{1n}) \\
 h_{21}\Delta p_1 + h_{22}\Delta p_2 + \cdots + h_{2n}\Delta p_n &= \Delta H_2 - (p_1\Delta h_{21} + p_2\Delta h_{22} + \cdots + p_n\Delta h_{2n}) \\
 &\vdots &&\vdots &&\vdots \\
 &\vdots &&\vdots &&\vdots \\
 h_{n1}\Delta p_1 + h_{n2}\Delta p_2 + \cdots + h_{nn}\Delta p_n &= \Delta H_n - (p_1\Delta h_{n1} + p_2\Delta h_{n2} + \cdots + p_n\Delta h_{nn})
 \end{aligned} \quad (10)$$

The delta terms in Eq. (10) are the magnitudes of the uncertainties of the various parameters. Equation (10) can be expressed in matrix algebra terms:

$$h \Delta p = \Delta H - (\Delta h) p \quad (11)$$

The matrices h and p are defined by Eqs. (4) and (5), respectively. The forms of the matrices Δh , Δp , and ΔH are analogous to Eqs. (4), (5), and (6), respectively. Multiplying Eq. (11) by h^{-1} gives

$$\Delta p = h^{-1} [\Delta H - (\Delta h) p] \quad (12)$$

where the quantity in brackets is an n -dimensional column vector.

After a set of partial pressure solutions has been calculated from Eq. (8), then Eq. (12) can be applied to evaluate the errors which are generated either by errors in groups of parameters or by an error in a single parameter. For example, assume that the errors in the sensitivity factors are zero, and that the mass spectrometer sensitivity drops to 90 percent of its calibrated sensitivity - a common occurrence when the mass spectrometer uses an electron multiplier for ion detection. In this case, all H_ℓ of an experimental spectrum will be 10 percent low, and Eq. (12) reduces to

$$\Delta p = -0.1 h^{-1} H \quad (13)$$

Therefore, from Eq. (8), the errors in the solutions are

$$\Delta p = -0.1 p \quad (14)$$

The conclusion in this case is that the accuracy of the solutions is the same as that of the peak height measurements. The accuracy of the peak height measurements depends largely on the ability of a mass spectrometer to hold its calibration.

If specific coefficients or constant terms are in error, rather than the entire H vector, the partial pressure solutions will contain errors whose magnitudes depend on the degree of ill-conditioning of the n chosen equations. These errors may be calculated from Eq. (12), which is employed later in applications of these analytical procedures.

2.2 AN ITERATION TECHNIQUE

Since data reduction by matrix inversion is rather tedious, a simpler procedure is needed. The following iteration technique promises to satisfy this need. First, all individual equations in the set of Eq. (2) that contain low sensitivity factors for all of the gases are deleted. This step is taken merely to avoid using very-low-level ion current peaks in the data reduction, because these low-level peaks are not usually measured accurately. Depending on the number of equations deleted, the resulting subset will contain r equations where $r \geq n$. Each equation will correspond to a specific mass number. Partial pressure solutions are then calculated as follows:

1. The first approximation, p_i' , to the true value of the i th partial pressure is taken as the smallest of the r values which are calculated from the following expression by letting ℓ vary through the r mass numbers:

$$p_i' = \frac{H_\ell}{h_{\ell i}} \quad (15)$$

2. Step (1) is repeated for $1 \leq i \leq n$ to obtain the first approximations to all of the n true solutions. Notice that each of these approximations will be greater than or equal to the corresponding true solution.
3. These approximations are substituted back into the subset of r equations and the spectrum, H_ℓ' , of these approximations is calculated.
4. An "error spectrum," E_ℓ , is calculated for the r mass numbers:

$$E_\ell = H_\ell - H_\ell' \quad (16)$$

Each current peak in this first error spectrum is negative or zero because $H_\ell' \geq H_\ell$ for each ℓ .

5. The partial pressures, e_i , of the error spectrum are approximated in a manner similar to step (1) above. That is, e_i is taken as the smallest of the r values which are calculated from the following expression by letting ℓ vary through the mass numbers:

$$e_i = \frac{|E_\ell|}{h_{\ell i}} \quad (17)$$

The proper sign to be attached to e_i is the sign of the specific value of E_ℓ which determined e_i .

6. Step (5) is repeated for $1 \leq i \leq n$ to obtain approximations of all partial pressures in the error spectrum.
7. The second set of approximations, p_i'' , to the true solutions of the subset of r equations is then calculated as:

$$p_i'' = p_i' + e_i \quad 1 \leq i \leq n \quad (18)$$

Each of these approximations will be less than or equal to the corresponding true solution.

8. Iterations are accomplished by repeating steps (3) through (7) until each current peak in the error spectrum becomes small compared to the corresponding peak in the experimental spectrum or until the error spectrum ceases to change with successive iterations.

Experimental evidence of convergence of this iterative procedure is presented for a specific 12-component mixture in section IV. It should be emphasized that the only acceptable evidence of convergence is that each current peak in the final error spectrum be small compared to the corresponding peak in the experimental spectrum.

A significant advantage of this iteration technique is that it is very simple to program and run on a computer.

SECTION III SPECTROMETER PERFORMANCE AND CALIBRATION DATA

The data reduction techniques outlined in the previous section involve two basic assumptions regarding mass spectrometer operation. First, linear operation according to Eqs. (1) and (2) is assumed, and secondly, the sensitivity factors calculated from Eq. (1) are assumed to remain constant until all experimental data are collected.

3.1 LINEARITY AND SENSITIVITY

The linearity and sensitivity of the Bendix 17-210V spectrometer are shown in Fig. 2. These data show the ion current peak height (i.e., the electron multiplier output) at mass 28 as a function of pure nitrogen (N_2) pressure for three different settings of electron multiplier voltage. The multiplier voltage is adjustable in 50-v steps from 1100 to 1600 v. A 50-v increase will increase the multiplier gain by a factor of approximately 2.1. A continuously variable gain control is also available for fine control of the multiplier gain at each setting of the multiplier voltage.

The nonlinearity of the 17-210V is caused primarily by a current saturation effect in the electron multiplier. Figure 2 shows that this saturation effect is evident over much of the operating range of the multiplier. The dashed lines show the desired, linear operation. The deviation from linear operation is current dependent and is larger at the larger currents. Extreme nonlinear operation is evident for current peaks exceeding about 4×10^{-8} amp. During partial pressure analyses, instrument operating parameters should be chosen to avoid generating peaks larger than this value.

The minimum detectable electrometer current is approximately 2×10^{-13} amp. Therefore, extrapolation of the data in Fig. 2 indicates that a multiplier voltage of 1600 v provides a minimum detectable N₂ partial pressure of approximately 1×10^{-11} torr. Also, at 1600 v the multiplier operation is approximately linear up to about 1.5×10^{-6} torr. Similarly, the minimum detectable N₂ partial pressure at 1350 v is about 2×10^{-10} torr, and the operation is approximately linear up into the 10^{-5} torr range. At 1100 v, the minimum detectable N₂ partial pressure is about 2×10^{-8} torr, and the operation is approximately linear up into the 10^{-5} torr range.

The data in Fig. 2 indicate that a multiplier voltage of 1350 v is best suited for vacuum measurements in the 1×10^{-9} to 1×10^{-5} torr range.

Figure 3 shows the data of Fig. 2 plotted in terms of the sensitivity factor for N₂ at mass 28 versus the N₂ pressure. These data show the extent of the variations in the instrument sensitivity for N₂.

In the present work, the multiplier was operated at 1350 v, and linear multiplier operation in the 1×10^{-12} to 1×10^{-9} amp range was assumed. During each calibration, a working standard partial pressure in the high 10^{-7} torr range was used, and the sensitivity factors were calculated from Eq. (1) at this single pressure.

In retrospect, it appears that the data from the 17-210V could have been completely linearized during data reduction by multiplying all current measurements by a current-dependent, experimentally determined correction factor. The feasibility of this procedure stems from the fact that the nonlinearity of the 17-210V originates in the multiplier and is dependent only on the current. This correction will be, in effect, another nonlinear stage of gain in the multiplier. Such corrections should be incorporated into the 17-210V data reduction procedures when the experimental data varies widely between 2×10^{-13} to 4×10^{-8} amp.

3.2 SENSITIVITY STABILITY

In addition to linearity, the instrument stability is of primary importance. Figure 4 shows the variations in the 17-210V sensitivity for N₂ (at mass 28) from day to day, over a 58-day period. These data were collected as follows: The instrument operating parameters were the same as listed in Fig. 2, and the multiplier was operated at 1350 v. Using the fine gain control, the multiplier gain was adjusted on the first day to give an N₂ sensitivity of exactly 10⁻³ amp/torr when the instrument was manually adjusted to mass 28. During most of the following days, the sensitivity was measured and then readjusted (standardized) to 10⁻³ amp/torr prior to starting each day's work. Figure 4 shows the measured sensitivity changes that occurred between successive standardizations. No standardization was accomplished during the intervals indicated by the dashed lines in Fig. 4.

During the 58-day period, the 17-210V was operated about 4 hr per day during analyses of mixtures consisting primarily of H₂O and CO₂ at a total pressure of 1 x 10⁻⁵ torr. Also, during this 58-day period, the ion source filament was hot about 10 hr per day, and the ion source pressure was maintained at about 1 x 10⁻⁹ torr except when an analysis was in progress.

The data of Fig. 4 show unpredictable sensitivity variations of up to 45 percent. These data serve only to point out that frequent, in-place checks and readjustments of the sensitivity are necessary for accurate partial pressure measurements. During the present work, this instrument standardization was always accomplished by first establishing an N₂ pressure of 10⁻⁶ torr in the ion source and then adjusting the fine multiplier gain to give 10⁻⁹ amp of multiplier current when manually adjusted to mass 28.

3.3 PARTIAL PRESSURE CALIBRATION DATA

Vacuum measurements by mass spectrometry require a considerable catalog of calibration data. All such 17-210V data accumulated during the present work are shown in Table I. These data are valid only for the 17-210V with operating parameters shown and with room temperature gases in the ion source region. As indicated previously, these data were calculated from Eq. (1) at a single test gas pressure in the high 10⁻⁷ torr range. The vacuum calibration system described in Ref. 1 was used to establish the absolute calibration pressures. The accuracies of these calibration pressures were ± 5 percent. Consequently, the accuracies of the sensitivity factors in Table I are also approximately ± 5 percent.

During the present 17-210V calibration efforts, it was found that the normalized 17-210V cracking pattern for each gas (i. e., sensitivity factors expressed as a percentage of the largest sensitivity factor) generally agreed with the cracking pattern data which are presented in the American Petroleum Institute (API) Research Project 44, Catalog of Mass Spectral Data. The API data were taken on the Consolidated Engineering Corporation Model 21-102 mass spectrometer.

SECTION IV EXPERIMENTAL EVALUATION OF DATA REDUCTION TECHNIQUES

In order to experimentally evaluate the data reduction techniques presented in sections 2.1 and 2.2, the vacuum calibration system was used to generate a working standard mixture of 12 common residual gases in the 17-210V ion source region. The type and partial pressure of each gas are given in the first two columns of Table II. The experimental, 17-210V spectrum of this mixture is given in Table III. As indicated previously, Eq. (2) for this mixture of gases is given by the set of equations in Fig. 1. The objective is to use this set of equations to reduce the spectrum in Table III. The partial pressure solutions obtained should compare favorably with the data in column 2 of Table II.

In order to employ the matrix inversion technique, the ill-conditioning of the equations of Fig. 1 must be considered. In accordance with previous discussion, only the equations in Fig. 1 which contain the larger sensitivity factors are considered for use in the data reduction (section 2.1.1). These are the 21 equations corresponding to mass numbers 2, 12, 14, 15, 16, 25, 26, 27, 28, 29, 30, 32, 37, 38, 39, 40, 41, 42, 43, 44, and 58. Although the equation corresponding to mass 12 contains small sensitivity factors, it is included because it provides additional information on carbon monoxide. The results of applying Eq. (9) to these 21 equations are given in Table IV. Only the $\cos^2\theta_{ij}$ terms which exceed 0.3 are tabulated.

Suppose an initial choice of 12 equations which correspond as closely as possible to the major peaks is made. This choice includes the equations from Fig. 1 corresponding to mass numbers 2, 14, 16, 27, 28, 29, 30, 32, 40, 41, 43, and 44. Table V lists those $\cos^2\theta_{ij}$ values from Table IV that apply to this initial system of 12 equations. Since the maximum $\cos^2\theta_{ij}$ value in Table V is 0.59, this initial choice is not as ill-conditioned as other possible choices. If the experimental spectrum (Table III) is reduced by matrix inversion, using this initial choice of equations, then the solutions in the third column of Table II

are obtained. The errors in these solutions relative to the working standard partial pressures are presented in column 4.

If an attempt is made to choose a better conditioned set of equations from Fig. 1, then the considerations outlined in section 2.1.1 lead to a final compromise consisting of the equations corresponding to mass numbers 2, 12, 16, 25, 28, 29, 30, 32, 40, 41, 43, and 44. Table VI lists the $\cos^2\theta_{ij}$ values from Table IV that apply to this final choice of equations. Since the maximum $\cos^2\theta_{ij}$ value in Table VI is 0.44, this final choice is somewhat less ill-conditioned than the initial choice. Reducing the experimental spectrum by matrix inversion of this final choice of equations yields the solutions presented in column 5 of Table II. Column 6 shows the errors in these solutions relative to the standard values.

If the iteration technique is employed to reduce the experimental spectrum (Table III), then the solutions in column 7, Table II, are obtained. Column 8 shows the errors in these solutions relative to the standards. The same 21 equations listed at the beginning of this section were employed in this iteration process. These are the equations which correspond to the mass numbers listed in column 1 of Table VII. Table VII is the computer data showing the error spectrum which was calculated during the tenth iteration. The process was stopped during the tenth iteration because the solutions and the error spectrum were not changing with successive iterations. Column 3 of Table VII shows the error spectrum, and column 4 shows the error spectrum expressed in percentage of the experimental spectrum at each mass number.

SECTION V DISCUSSION OF EXPERIMENTAL RESULTS

Since the same vacuum calibration system was used both to calibrate the mass spectrometer and to generate the working standard 12-component mixture, the partial pressure solutions in Table II should agree with the standard values to within approximately ± 3 percent. This ± 3 percent is the estimated reproducibility of working standard partial pressures in the vacuum calibration system.

A study of Table II indicates that the most accurate set of solutions is the set obtained by the iteration technique. However, the solutions for Ar, CO₂, CO, and CH₂CH₂ are in considerable error in all three sets of solutions. Although it was not possible to conclusively identify the sources of these errors, certain observations were made. Specifically,

the working standard partial pressure values were substituted into the equations of Fig. 1, and exact H_f values were calculated. Several resulting peak heights are listed in column 2 of Table VIII. Column 3 of Table VIII shows the experimental values (Table III), and column 4 shows the percentage of difference of each experimental peak relative to the exact calculated value. The data in Table VIII show that the differences between the experimental and the calculated values at mass numbers 40 and 44 are nearly the same as the errors in the solutions listed in Table II for Ar and CO₂, respectively. This indicates either that the Ar and CO₂ sensitivity factors in Fig. 1 are in error or that the working standard partial pressures are in error. The former is considered to be more probable.

The two best solutions for CO in Table II are considered to be the one obtained by the matrix inversion of the better conditioned set of equations and the one obtained by iteration (columns 5 and 7, Table II). The fact that these two solutions are in agreement suggests that additional CO was generated by reactions of gases in the mixture with the ion source filament.

The conclusion from this exercise is that the iteration technique yields more accurate partial pressure solutions than those obtained by matrix inversion. One reason for this appears to be that the iteration technique uses more of the experimental data from each spectrum than does the matrix inversion technique.

SECTION VI DISCUSSION OF SOURCES OF ERROR

In general, the most significant errors in absolute partial pressure solutions result from three sources: calibration errors, changes of instrument sensitivity after calibration, and inconsistencies in the experimental data.

If the original working standard partial pressure against which the spectrometer is calibrated is in error, then all the sensitivity factors calculated from Eq. (1) will be in error by the negative of the same amount; consequently, all solutions which are calculated using these sensitivity factors will be in error by the same amount as the original standard partial pressure.

The mass spectrometer sensitivity may change by a certain percentage for all gases because of changes in multiplier gain or in ionizing

current. If the sensitivity changes by a certain percentage, then all of the elements in the H vector, Eq. (6), and the partial pressure solutions for all the gases will be in error by the same percentage (section 2.1.2).

Inconsistencies may exist in a set of calibration data and/or in an experimental spectrum. Inconsistent data are characterized by varying errors in the sensitivity factors of a gas or in the elements of the H vector. Inconsistencies in the data can generate large, unpredictable errors in one or more of the solutions (section 6.1). Inconsistencies may be introduced into the data in several ways:

- a. The working standard partial pressure against which the mass spectrometer is calibrated, or the partial pressures of gases in the mixture being analyzed, may change slightly during the mass spectrum scan.
- b. The electron multiplier used for ion detection and/or the current electrometer may not operate linearly over the entire range of the ion current measurements (section 3.1).
- c. The normalized cracking pattern for a pure gas may change slightly depending on the condition of the ion source filament and on the degree of contamination of the ion source. To illustrate the symptom of this source of error, Table IX shows two sets of normalized, 17-210V cracking patterns for ten gases. These calibration data were run under apparently identical conditions (operating parameters same as listed in Table I) except that after completing set 1 and before starting set 2, the 17-210V ion source was cleaned, and a new ion source filament and a new multiplier dynode were installed.
- d. Reading errors in single peaks may occur inadvertently; this is very likely in manual data processing.

6.1 EFFECTS OF INCONSISTENT DATA

Calibration errors and errors caused by changes of instrument sensitivity are easily dealt with by performing accurate calibrations and frequent checks of the sensitivity. However, inconsistencies in the data are unpredictable and can generate solution errors much greater than the magnitude of the inconsistencies. This fact is illustrated by the following exercise. First, assume that a mixture is composed of the partial pressures in column 2 of Table X and then calculate the exact spectrum of the mixture by substituting the assumed solutions into the equations of Fig. 1. When small errors

are introduced into this calculated spectrum at mass numbers 14, 27, 28, and 29, it is found that the calculated solutions are most sensitive to an inconsistency in the spectrum at mass 29 (H_{29}). Specifically, H_{29} in the calculated spectrum is 7.164×10^{-10} amp. Suppose an inconsistency is introduced into the spectrum by changing this value to 7.307×10^{-10} amp. This is an error of 2 percent in H_{29} . The resulting errors which are generated in the partial pressure solutions may be calculated from Eq. (12). From Eq. (10) it will be noticed that this 2-percent error can be interpreted either as an error in H_{29} or as an error in one of the sensitivity factors. At any rate, if an h^{-1} is calculated using the equations from Fig. 1 corresponding to mass numbers 2, 14, 16, 27, 28, 29, 30, 32, 40, 41, 43, and 44 (i.e., the initial choice of section IV), and if the matrix multiplication of Eq. (12) is carried out, then the Δp of column 3, Table X, are obtained. Column 4 shows these errors expressed as percentages of the assumed solutions. Reducing the spectrum containing the 2-percent error in H_{29} by the iteration technique yields the solutions in column 5 of Table X. Column 6 shows the errors in these solutions relative to the assumed solutions.

A comparison of columns 4 and 6, Table X, suggests that solutions obtained by the iteration technique are not affected by inconsistent data as much as are the solutions obtained by matrix inversion.

If a set of mass spectrometer data is greatly inconsistent, then it is possible to obtain negative values for partial pressure solutions when reducing the data by matrix inversion.

6.2 ACCURACY OF PARTIAL PRESSURE MEASUREMENTS

If inconsistent data are avoided by proper experimental technique, and if the best data reduction techniques are employed, the accuracies of partial pressure measurements will be determined primarily by the accuracies of the original partial pressures used for calibration and by the extent to which the mass spectrometer sensitivity varies. Absolute partial pressures and, consequently, the sensitivity factors of Eq. (1) may be established to within approximately ± 5 percent (Ref. 1).

Figure 4 indicates that, in general (74 percent of the data points), the 17-210V sensitivity remains constant to within ± 10 percent for short periods. However, to realize this constant (± 10 percent) sensitivity in long-term, routine measurement activities, the mass spectrometer installation must include an in-place calibration capability. Instrument standardization can then be accomplished quickly using a single test gas.

The magnitudes of these two major sources of error indicate that it is possible to make absolute partial pressure measurements routinely with an accuracy of ± 15 percent. Two-thirds of this error is caused by random changes in instrument sensitivity. Under some operating conditions this ± 10 -percent error could be reduced by frequent instrument standardization.

SECTION VII CONCLUSIONS

The experimental results show that random changes in the sensitivity of the Bendix 17-210V time-of-flight mass spectrometer occur during long-term operations in high vacuum. Therefore, any installation of the 17-210V must include in-place partial pressure calibration equipment, when accurate, absolute, partial pressure measurements are required. With such equipment, the instrument sensitivity can be maintained constant to within ± 10 percent by readjusting the multiplier gain on a day-to-day basis. This standardization can be accomplished conveniently using a single test gas at one partial pressure setting.

Calibrations for all gases of interest should be repeated often, in order to ensure consistent data. The required calibration interval will depend greatly on the vacuum conditions to which the ion source is exposed and cannot be specified on the basis of the present work.

The matrix inversion data reduction technique is more difficult to apply than the iteration technique because the ill-conditioning of the subset of equations that is used must be considered and because the inverse of the coefficient matrix must be calculated. The solutions obtained by the matrix inversion technique are more affected by inconsistencies in the data than are the solutions obtained by iteration. However, the convergence of the iteration technique is not certain and must be demonstrated by an application of the technique to the experimental data. The present experimental results indicate that if the data are consistent, then the iterations will converge. The computer program of the iteration procedure is simple, and, in general, the results indicate that the iteration technique is the more satisfactory technique for calculating absolute partial pressures from mass spectrometer data.

Finally, calculated partial pressure solutions are unusually sensitive to inconsistencies in the experimental data, and poor experimental technique can easily result in large errors in the solutions. If inconsistent data are carefully avoided, then partial pressure measurement accuracies of ± 15 percent or better are obtainable by time-of-flight mass spectrometry.

APPENDIX I
CALCULATION OF THE INVERSE OF THE COEFFICIENT MATRIX

During the present work, the inverse of the coefficient matrix was calculated by an application of the modified Sherman-Morrison technique (Ref. 6). Basically, this technique is concerned with the calculation of the inverse of a n -dimension matrix after adjustments are made in the elements of a row or a column of the matrix. This calculation requires the inverse of the matrix before the adjustments are made. The inverse of the adjusted matrix is given by (Ref. 7):

$$(H + ue_i^T)^{-1} = H^{-1} - \frac{(H^{-1}u)(e_i^T H^{-1})}{1 + e_i^T H^{-1}u} \quad (I-1)$$

where H = the original matrix

H^{-1} = the inverse of the original matrix

$(H + ue_i^T)$ = the adjusted matrix

e_i^T = a row vector which is given by the transpose of the i th column of the identity matrix (I).

u = the column vector which is added to the i th column of H . The vector u is defined so that this addition yields the desired adjusted matrix.

In the present work, Eq. (I-1) was programmed on the computer and was applied repeatedly to obtain the inverse of the coefficient matrix, h . The general procedure is as follows: First, a matrix, h_0 , whose inverse is easily calculated is defined. A convenient h_0 is the diagonal matrix of h . If any of the diagonal elements of h are zero, they are replaced by 1 in the construction of h_0 . The inverse of h_0 is easily calculated, since its diagonal elements are simply the reciprocals of the diagonal elements of h_0 . Next, the coefficient matrix, h , is decomposed as follows:

$$\begin{aligned} h_1 &= h_0 + u_1 e_1^T \\ h_2 &= h_1 + u_2 e_2^T \\ &\vdots &&\vdots \\ &\vdots &&\vdots \\ &\vdots &&\vdots \\ h_n &= h_{n-1} + u_n e_n^T \end{aligned} \quad (I-2)$$

where

$$u_i = (h - h_0) e_i \quad i = 1, 2, \dots, n \quad (I-3)$$

The vector e_i is a column vector corresponding to the i th column of the identity matrix. Since h_n in Eq. (I-2) is equal to the coefficient matrix, h , the repeated application of Eq. (I-1) to h_1, h_2, \dots, h_n in Eq. (I-2) yields h_n^{-1} , which (except for possible round-off errors) is the desired h^{-1} .

The h_n^{-1} matrix calculated by the above procedure may be in error as a result of round-off errors in the computer. Therefore, after completion of the above procedure, additional computations were performed to improve the accuracy of the calculated inverse. The basis for these additional calculations is as follows. For the sake of simplicity, let the calculated value of the matrix h_n^{-1} be designated by the symbol d_0^{-1} . Since d_0^{-1} is not the perfect inverse of h_n , a matrix F_0 can be calculated (Ref. 8):

$$F_0 = I - h_n d_0^{-1} \quad (I-4)$$

The following sequence of matrices can then be formed:

$$\begin{aligned} d_1^{-1} &= d_0^{-1} (I + F_0) \\ d_2^{-1} &= d_1^{-1} (I + F_1) \\ &\vdots && \vdots \\ &\vdots && \vdots \\ &\vdots && \vdots \\ d_{m-1}^{-1} &= d_{m-2}^{-1} (I + F_{m-1}) \end{aligned} \quad (I-5)$$

where

$$\begin{aligned} F_1 &= (I - h_n d_1^{-1}) \\ F_2 &= (I - h_n d_2^{-1}) \\ &\vdots && \vdots \\ &\vdots && \vdots \\ F_{m-1} &= (I - h_n d_{m-1}^{-1}) \end{aligned} \quad (I-6)$$

Faddeeva shows that each successive inverse matrix, $d_1^{-1}, d_2^{-1}, \dots, d_{m-1}^{-1}$ is a more accurate estimate of h_n^{-1} (and consequently h^{-1}) than the preceding one (Ref. 8). In the present work, d_1^{-1} was taken to be the inverse of the coefficient matrix, since the calculation of d_2^{-1} was found to provide negligible corrections.

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$1.52^{-5}P_2^+$	0	+	0	$+1.96^{-5}P_5 + 2.07^{-5}P_6^+$	0	+	0	$+1.95^{-5}P_9 + 1.31^{-5}P_{10}^+$	0	+	$+6.86^{-5}P_{12} = H_1$
$4.65^{-4}P_1 + 9.00^{-6}P_2^+$	0	+	0	$+2.99^{-6}P_5 - 7.32^{-6}P_6^+$	0	+	0	$+4.98^{-6}P_9 - J.75^{-6}P_{10}^+$	0	+	$+1.85^{-5}P_{12} = H_2$
$1.89^{-5}P_2 + 3.88^{-5}P_3^+$	0	+	0	$+1.31^{-5}P_5 + 6.69^{-6}P_6^+$	0	+	0	$+8.26^{-6}P_9 + 2.86^{-6}P_{10}^+ + 4.63^{-5}P_{11} + 9.23^{-7}P_{12} = H_{12}$			
$5.86^{-5}P_2^+$	0	+	0	$+2.65^{-5}P_5 + 1.43^{-5}P_6^+$	0	+	0	$+1.53^{-5}P_9 + 8.66^{-6}P_{10}^+$	0	+	$+2.64^{-5}P_{12} = H_{13}$
$1.28^{-4}P_2 + 4.70^{-6}P_3 + 6.39^{-5}P_4 + 5.13^{-5}P_5 + 4.61^{-5}P_6^+$	0	+	0	$+3.75^{-5}P_9 - 2.77^{-5}P_{10}^+$	0	+	0	$+1.48^{-5}P_{12} = H_{14}$			
$7.45^{-4}P_2^+$	0	+	0	$+5.13^{-6}P_5 + 6.56^{-5}P_6^+$	0	+	0	$+5.70^{-5}P_9 + 8.38^{-5}P_{10}^+$	0	+	$+7.63^{-5}P_{12} = H_{15}$
$1.01^{-3}P_2 + 1.88^{-5}P_3^+$	0	+	0	$+3.18^{-6}P_6 + 8.81^{-5}P_7^+$	0	+	$+1.97^{-6}P_9 + 2.86^{-6}P_{10} + 9.68^{-5}P_{11} + 1.72^{-6}P_{12} = H_{16}$				
				$2.53^{-5}P_9 + 1.14^{-5}P_{10}^+$	0	+	0				$= H_{18}$
				$1.56^{-5}P_9 + 7.05^{-8}P_{10}^+$	0	+	0				$= H_{19,5}$
				$6.34^{-5}P_8 + 1.86^{-5}P_9 + 1.26^{-5}P_{10}^+$	0	+	0				$= H_{20}$
				$1.13^{-5}P_{11}^+$	0						$= H_{22}$
				$3.24^{-5}P_5 + 1.15^{-5}P_6^+$	0	+	0	$+5.77^{-6}P_9 + 1.79^{-6}P_{10}^+$	0	+	$= H_{24}$
				$9.94^{-5}P_5 + 6.05^{-5}P_6^+$	0	+	0	$+2.78^{-5}P_9 + 1.22^{-5}P_{10}^+$	0	+	$+7.78^{-6}P_{12} = H_{25}$
				$5.13^{-4}P_5 + 3.34^{-4}P_6^+$	0	+	0	$+1.14^{-4}P_9 + 1.25^{-4}P_{10}^+$	0	+	$+8.66^{-5}P_{12} = H_{26}$
				$5.42^{-4}P_5 + 4.83^{-4}P_6^+$	0	+	0	$+3.56^{-4}P_9 + 5.11^{-4}P_{10}^+$	0	+	$+4.89^{-4}P_{12} = H_{27}$
$1.09^{-3}P_3 + 9.23^{-4}P_4 + 8.90^{-4}P_5 + 1.54^{-3}P_6 + 8.90^{-6}P_7^+$	0	+	0	$+2.91^{-5}P_9 + 7.69^{-4}P_{10} + 7.48^{-5}P_{11} + 4.49^{-4}P_{12} = H_{28}$							
$1.20^{-5}P_3 + 7.45^{-6}P_4 + 2.03^{-5}P_5 + 3.25^{-4}P_6^+$	0	+	0	$+4.52^{-3}P_6^+$	0	+	0	$+1.21^{-3}P_{10}^+$	0	+	$+5.84^{-4}P_{12} = H_{29}$
				$1.08^{-5}P_6^+$	0	+	0	$+3.14^{-5}P_{10}^+$	0	+	$+1.54^{-5}P_{12} = H_{30}$
				$7.80^{-4}P_7^+$	0	+	0	$+8.53^{-7}P_{11} + 1.72^{-6}P_{12} = H_{32}$			
				$2.79^{-6}P_8 + 2.91^{-5}P_9 + 7.05^{-6}P_{10}^+$	0	+	$+1.72^{-6}P_{12} = H_{36}$				
				$1.42^{-4}P_9 + 5.06^{-5}P_{10}^+$	0	+	$+1.88^{-5}P_{12} = H_{37}$				
				$2.07^{-4}P_9 + 8.13^{-5}P_{10}^+$	0	+	$+3.98^{-5}P_{12} = H_{38}$				
				$7.46^{-4}P_9 + 2.56^{-4}P_{10}^+$	0	+	$+2.03^{-4}P_{12} = H_{39}$				
				$9.04^{-4}P_8 + 2.91^{-4}P_9 + 4.15^{-5}P_{10}^+$	0	+	$+3.21^{-5}P_{12} = H_{40}$				
				$1.10^{-3}P_8 + 1.80^{-4}P_{10}^+$	0	+	$+4.00^{-4}P_{12} = H_{41}$				
				$7.97^{-4}P_9 + 7.88^{-5}P_{10}^+$	0	+	$+1.89^{-4}P_{12} = H_{42}$				
				$3.17^{-5}P_9 + 3.48^{-4}P_{10}^+$	0	+	$+1.33^{-3}P_{12} = H_{43}$				
				$3.54^{-6}P_9 + 5.10^{-4}P_{10} + 9.96^{-4}P_{11} + 8.27^{-5}P_{12} = H_{44}$							
PARTIAL PRESSURE LEGEND,								$1.63^{-5}P_{10} + 1.22^{-5}P_{11}^+$	0	+	$= H_{45}$
P_1 - Hydrogen, H_2								$5.91^{-6}P_{11}^+$	0	+	$= H_{46}$
P_2 - Methane, CH_4								$6.86^{-6}P_{12} = H_{49}$			
P_3 - Carbon Monoxide, CO								$2.05^{-5}P_{12} = H_{50}$			
P_4 - Nitrogen, N_2								$1.75^{-5}P_{12} = H_{51}$			
P_5 - Ethylene, $CH_2 : CH_2$								$4.62^{-6}P_{12} = H_{52}$			
P_6 - Ethane, CH_3CH_3								$1.35^{-5}P_{12} = H_{53}$			
P_7 - Oxygen, O_2								$4.09^{-6}P_{12} = H_{54}$			
P_8 - Argon, Ar								$1.67^{-5}P_{12} = H_{55}$			
P_9 - Propene, $CH_2 : CHCH_3$								$1.37^{-5}P_{12} = H_{56}$			
P_{10} - Propane, $CH_3CH_2CH_3$								$4.75^{-6}P_{12} = H_{57}$			
P_{11} - Carbon Dioxide, CO_2								$2.90^{-4}P_{12} = H_{58}$			
P_{12} - Butane, $CH_3(CH_2)_2CH_3$								$1.54^{-5}P_{12} = H_{59}$			

Fig. 1 Calibration of Bendix 17-210V Mass Spectrometer

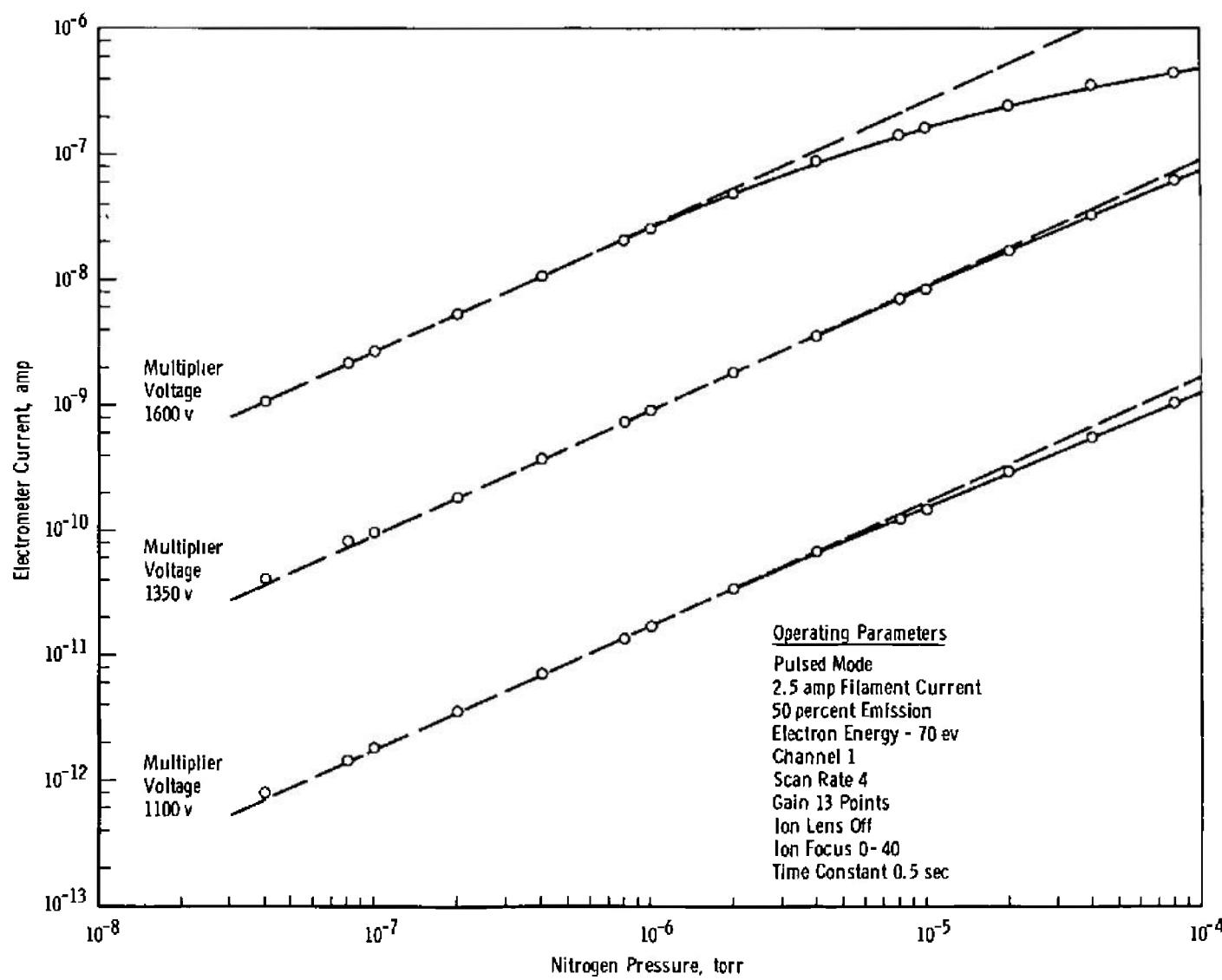


Fig. 2 Bendix 17-210V Calibration for Nitrogen at Mass No. 28

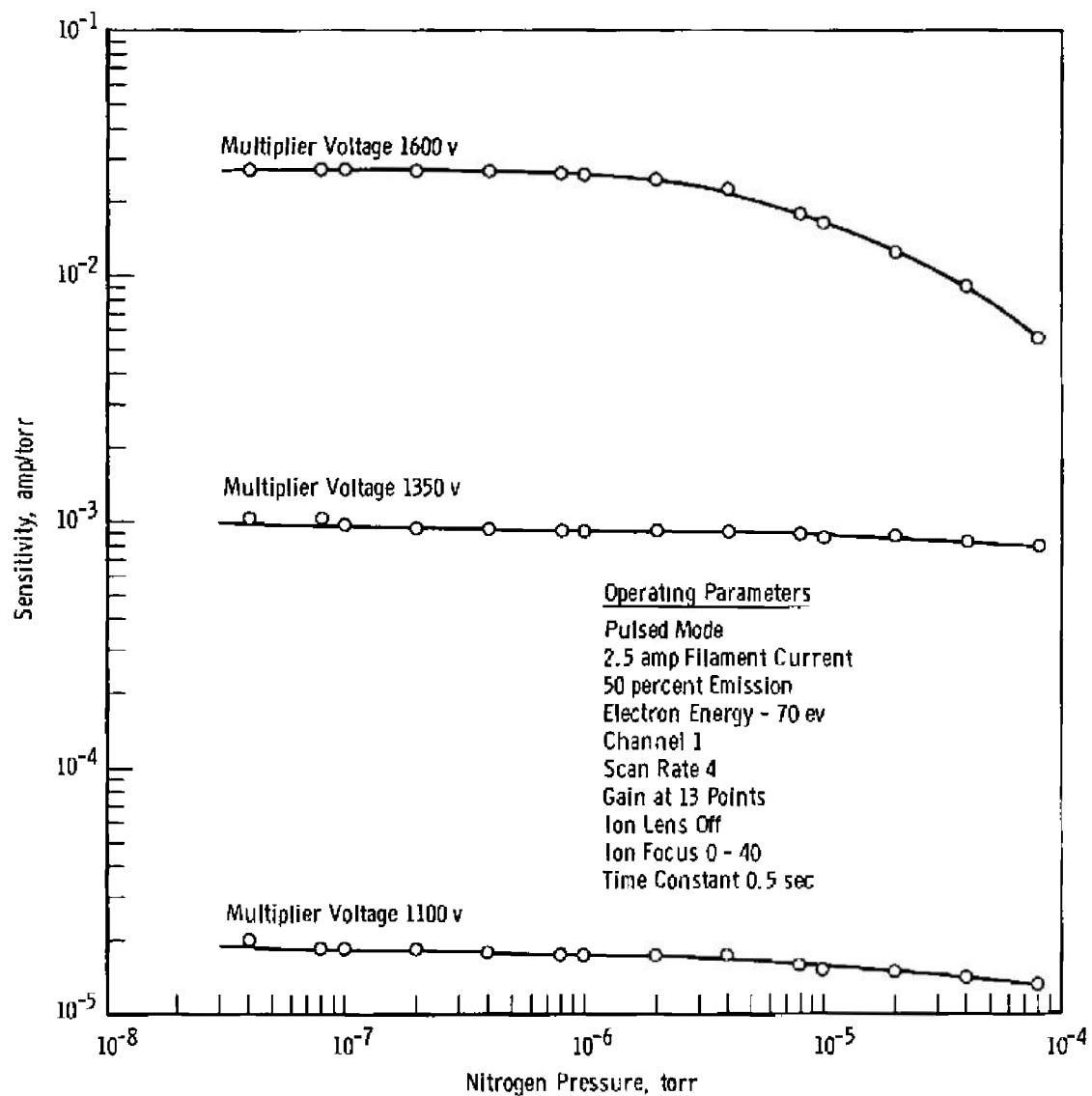


Fig. 3 Bendix 17-210V Sensitivity for Nitrogen at Mass No. 28 versus Nitrogen Pressure

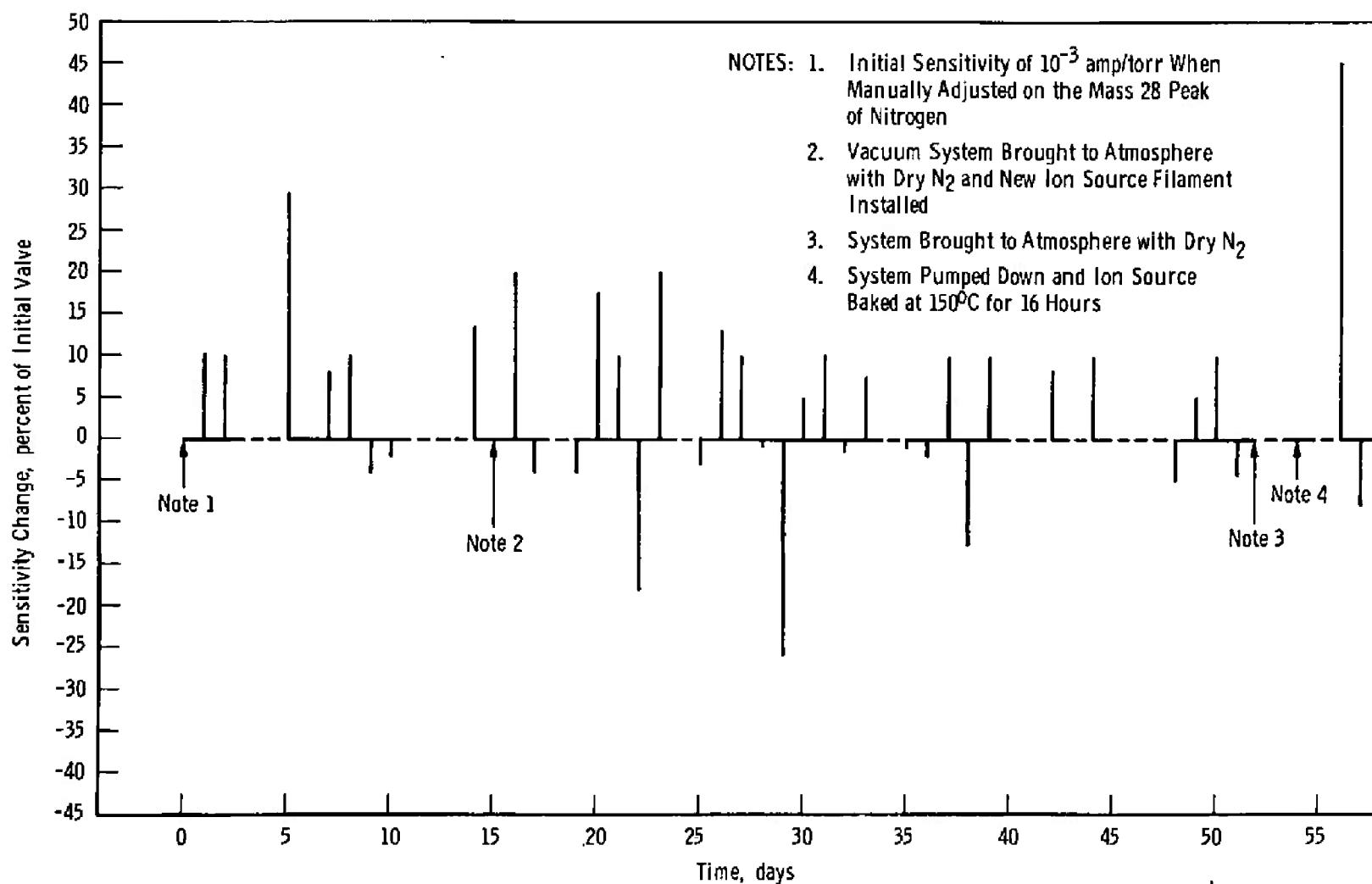


Fig. 4 Bendix 17-210V Sensitivity versus Time

TABLE I
BENDIX 17-210V CALIBRATION DATA

Carbon Tetrachloride CCl_4		Propane $\text{CH}_3\text{CH}_2\text{CH}_3$		Tetrachloro- ethylene CCl_2CCl_2		Ethanol $\text{CH}_3\text{CH}_2\text{OH}$		Normal Pentane $\text{CH}_3(\text{CH}_2)_3\text{CH}_3$	
Mass No.	amp/torr	Mass No.	amp/torr	Mass No.	amp/torr	Mass No.	amp/torr	Mass No.	amp/torr
12	3.66×10^{-5}	1	1.31×10^{-5}	12	2.89×10^{-5}	1	1.64×10^{-5}	1	1.44×10^{-5}
27	2.03×10^{-6}	2	3.75×10^{-6}	24	4.91×10^{-5}	2	7.45×10^{-6}	14	7.78×10^{-6}
29	2.03×10^{-6}	13	8.66×10^{-6}	35	1.28×10^{-4}	12	1.19×10^{-5}	15	6.20×10^{-5}
31	2.03×10^{-8}	14	2.77×10^{-5}	37	3.93×10^{-5}	13	2.53×10^{-5}	26	5.48×10^{-5}
35	1.63×10^{-4}	15	8.38×10^{-5}	47	1.92×10^{-4}	14	6.56×10^{-5}	27	4.40×10^{-4}
37	5.18×10^{-5}	16	2.86×10^{-6}	48	6.07×10^{-5}	15	1.19×10^{-4}	28	1.12×10^{-4}
41	4.06×10^{-6}	19	1.14×10^{-5}	58	9.65×10^{-5}	16	1.19×10^{-5}	29	3.00×10^{-4}
42	2.03×10^{-6}	19.5	7.05×10^{-6}	61	3.18×10^{-5}	17	1.49×10^{-5}	30	1.15×10^{-5}
43	1.63×10^{-6}	20	1.26×10^{-5}	82	5.49×10^{-5}	18	1.94×10^{-5}	37	1.15×10^{-5}
47	1.74×10^{-4}	24	1.79×10^{-6}	83	5.78×10^{-5}	19	4.17×10^{-5}	38	3.31×10^{-5}
49	5.49×10^{-5}	25	1.22×10^{-5}	84	3.56×10^{-5}	24	7.45×10^{-6}	39	2.15×10^{-4}
58.5	1.22×10^{-5}	26	1.25×10^{-4}	85	2.31×10^{-5}	25	2.98×10^{-5}	40	4.03×10^{-5}
59.5	1.22×10^{-6}	27	5.11×10^{-4}	94	1.62×10^{-4}	26	1.15×10^{-4}	41	5.33×10^{-4}
60.5	4.06×10^{-6}	28	7.69×10^{-4}	96	1.02×10^{-4}	27	2.71×10^{-4}	42	7.91×10^{-4}
70	8.10×10^{-6}	29	1.21×10^{-3}	98	1.73×10^{-5}	28	7.00×10^{-5}	43	1.27×10^{-3}
72	4.06×10^{-6}	30	3.14×10^{-5}	119	2.89×10^{-8}	29	2.83×10^{-4}	44	4.47×10^{-5}
74	8.13×10^{-7}	36	7.05×10^{-6}	121	2.89×10^{-6}	30	7.45×10^{-5}	50	1.01×10^{-5}
82	1.24×10^{-4}	37	5.06×10^{-5}	129	1.85×10^{-4}	31	1.15×10^{-3}	51	1.15×10^{-5}
84	8.01×10^{-5}	38	8.13×10^{-5}	131	1.82×10^{-4}	32	1.64×10^{-5}	53	1.44×10^{-5}
86	1.30×10^{-5}	39	2.56×10^{-4}	133	6.24×10^{-5}	41	1.49×10^{-5}	55	4.18×10^{-5}
117	3.91×10^{-4}	40	4.15×10^{-5}	135	6.67×10^{-8}	42	4.17×10^{-5}	56	3.46×10^{-5}
119	3.74×10^{-4}	41	1.80×10^{-4}	164	3.18×10^{-4}	43	1.04×10^{-4}	57	1.67×10^{-4}
121	1.20×10^{-4}	42	7.58×10^{-5}	166	4.02×10^{-4}	44	1.49×10^{-5}	58	1.01×10^{-5}
123	1.42×10^{-5}	43	3.48×10^{-4}	168	1.92×10^{-4}	45	4.10×10^{-4}	71	1.30×10^{-5}
		44	5.10×10^{-4}	170	4.16×10^{-5}	46	3.06×10^{-4}	72	1.57×10^{-4}
		45	1.63×10^{-5}			47	1.19×10^{-5}	73	1.15×10^{-5}
Hydrogen H_2		Hydrogen Fluoride HF		Oxygen O_2		Helium He		Carbon Monoxide CO	
Mass No.	amp/torr	Mass No.	amp/torr	Mass No.	amp/torr	Mass No.	amp/torr	Mass No.	amp/torr
2	4.65×10^{-4}	18	1.81×10^{-2}	19	1.47×10^{-2}	18	8.81×10^{-5}	4	1.39×10^{-4}
						28	8.90×10^{-8}		
						32	7.80×10^{-4}		
Methane CH_4		Argon Ar		Water H_2O		Nitrogen N_2		Carbon Monoxide CO	
Mass No.	amp/torr	Mass No.	amp/torr	Mass No.	amp/torr	Mass No.	amp/torr	Mass No.	amp/torr
1	1.52×10^{-5}	20	8.34×10^{-5}	16	2.8×10^{-5}	12	3.88×10^{-5}	12	3.88×10^{-5}
2	9.00×10^{-6}	36	2.79×10^{-6}	17	2.03×10^{-4}	14	6.39×10^{-5}	14	4.70×10^{-6}
12	1.68×10^{-5}	40	9.04×10^{-4}	18	7.67×10^{-4}	28	9.23×10^{-4}	18	1.88×10^{-5}
13	5.86×10^{-5}			19	2.6×10^{-6}	29	7.45×10^{-6}	28	1.09×10^{-3}
14	1.26×10^{-4}							29	1.20×10^{-5}
15	7.45×10^{-4}								
16	1.91×10^{-3}								

OPERATING PARAMETERS:

Pulsed Mode of Operation
 Filament Current 2.5 amps
 Ionizing Potential: 70 Electron volts
 Trap Current: 50 percent of Full Scale
 Ion Lens Off
 Ion Focus 0 - 40
 Scan Rate 4
 Channel 1
 Multiplier Voltage. 1350 volts
 Gain Adjusted for Nitrogen Sensitivity of
 10^{-3} amp/torr when Manually Adjusted
 to Mass No. 28 and with Calibration
 Pressure of $1 \cdot 10^{-6}$ torr.

TABLE I (Continued)

Butane $\text{CH}_3(\text{CH}_2)_2\text{CH}_3$		Toluene $\text{C}_6\text{H}_5\text{CH}_3$		Methyl Ethyl Ketone $\text{CH}_3\text{COCH}_2\text{CH}_3$		1,1-Dichloroethane CH_3CHCl_2		Isopropyl Alcohol $\text{CH}_3\text{CH(OH)CH}_3$		Propene $\text{CH}_2=\text{CHCH}_3$	
Mass No.	amp/torr	Mass No.	amp/torr	Mass No.	amp/torr	Mass No.	amp/torr	Mass No.	amp/torr	Mass No.	amp/torr
1	6.86×10^{-6}	1	1.15×10^{-5}	1	9.07×10^{-6}	1	7.09×10^{-6}	1	9.12×10^{-6}	1	1.95×10^{-6}
2	1.85×10^{-6}	14	1.15×10^{-5}	13	1.45×10^{-5}	12	5.67×10^{-6}	2	4.98×10^{-6}	2	4.98×10^{-6}
12	9.23×10^{-7}	15	2.88×10^{-5}	14	5.44×10^{-5}	13	8.51×10^{-6}	12	8.26×10^{-6}	12	8.26×10^{-6}
13	2.64×10^{-6}	26	4.75×10^{-5}	15	2.20×10^{-4}	14	9.22×10^{-6}	13	1.53×10^{-5}	13	1.53×10^{-5}
14	1.48×10^{-5}	27	9.35×10^{-5}	18	9.07×10^{-6}	15	1.49×10^{-5}	14	3.75×10^{-5}	14	3.75×10^{-5}
15	7.63×10^{-5}	31	1.15×10^{-5}	25	1.45×10^{-5}	24	9.93×10^{-6}	15	5.70×10^{-5}	15	5.70×10^{-5}
16	1.72×10^{-6}	37	5.47×10^{-5}	26	9.44×10^{-5}	25	4.68×10^{-5}	16	1.97×10^{-6}	16	1.97×10^{-6}
25	7.78×10^{-6}	38	9.50×10^{-5}	27	2.74×10^{-4}	26	1.82×10^{-4}	19	8.36×10^{-5}	19	2.53×10^{-5}
28	9.66×10^{-5}	39	3.08×10^{-4}	28	5.44×10^{-5}	28	3.55×10^{-5}	25	7.60×10^{-6}	19.5	1.56×10^{-5}
27	4.89×10^{-4}	40	4.60×10^{-5}	29	4.17×10^{-4}	35	5.74×10^{-5}	26	3.80×10^{-5}	20	1.86×10^{-5}
28	4.49×10^{-4}	41	3.74×10^{-5}	30	1.07×10^{-5}	36	1.92×10^{-5}	27	2.20×10^{-4}	24	5.77×10^{-6}
29	5.84×10^{-4}	43	5.76×10^{-5}	31	9.07×10^{-6}	37	2.13×10^{-5}	28	1.82×10^{-5}	25	2.78×10^{-5}
30	1.54×10^{-5}	44	1.73×10^{-5}	37	1.81×10^{-5}	47	2.27×10^{-5}	30	1.52×10^{-5}	26	1.14×10^{-4}
32	1.72×10^{-6}	45	7.62×10^{-5}	38	1.81×10^{-5}	48	1.56×10^{-5}	31	7.60×10^{-5}	27	3.56×10^{-4}
36	1.72×10^{-6}	45.5	5.61×10^{-5}	39	4.72×10^{-5}	49	1.08×10^{-5}	36	3.04×10^{-6}	28	2.81×10^{-5}
37	1.98×10^{-5}	46	6.47×10^{-5}	41	3.99×10^{-5}	59	6.38×10^{-6}	37	2.28×10^{-5}	36	2.91×10^{-5}
38	3.98×10^{-5}	49	2.88×10^{-5}	42	1.09×10^{-4}	60	2.13×10^{-5}	38	3.19×10^{-5}	37	1.42×10^{-4}
39	2.03×10^{-4}	50	1.21×10^{-4}	43	1.63×10^{-3}	61	5.82×10^{-5}	39	8.42×10^{-5}	38	2.07×10^{-4}
40	3.21×10^{-5}	51	1.70×10^{-4}	44	4.54×10^{-5}	62	5.74×10^{-5}	40	1.52×10^{-5}	39	7.46×10^{-4}
41	4.00×10^{-4}	52	5.04×10^{-5}	45	1.81×10^{-5}	63	8.36×10^{-4}	41	1.05×10^{-4}	40	2.91×10^{-4}
42	1.89×10^{-4}	53	2.73×10^{-5}	49	9.07×10^{-6}	64	3.55×10^{-5}	42	6.84×10^{-5}	41	1.10×10^{-3}
43	1.33×10^{-3}	61	4.60×10^{-5}	50	1.81×10^{-5}	65	2.13×10^{-4}	43	2.86×10^{-4}	42	7.97×10^{-5}
44	8.27×10^{-5}	62	8.63×10^{-5}	51	9.07×10^{-6}	83	8.01×10^{-5}	44	1.02×10^{-4}	43	3.17×10^{-5}
49	6.86×10^{-6}	63	1.65×10^{-4}	53	9.07×10^{-6}	85	5.04×10^{-5}	45	1.48×10^{-3}	44	3.54×10^{-6}
50	2.05×10^{-5}	84	5.47×10^{-5}	55	1.09×10^{-5}	87	7.09×10^{-6}	46	4.26×10^{-4}		
51	1.75×10^{-6}	85	1.98×10^{-4}	56	9.07×10^{-6}	98	8.86×10^{-5}	47	7.60×10^{-6}		
52	4.52×10^{-6}	66	4.32×10^{-5}	57	1.12×10^{-4}	100	5.53×10^{-5}	57	7.51×10^{-6}		
53	1.35×10^{-5}	74	2.30×10^{-5}	58	1.09×10^{-5}	102	7.80×10^{-8}	59	5.40×10^{-5}		
54	4.09×10^{-6}	75	1.73×10^{-5}	71	2.36×10^{-5}			60	1.95×10^{-5}		
55	1.87×10^{-5}	77	2.30×10^{-5}	72	2.63×10^{-4}						
56	1.37×10^{-5}	85	1.44×10^{-5}	86	2.01×10^{-5}						
57	4.75×10^{-5}	87	1.44×10^{-5}	89	6.33×10^{-5}						
58	2.90×10^{-4}	90	5.76×10^{-5}	91	1.30×10^{-3}						
59	1.54×10^{-5}	92	1.31×10^{-3}	93	1.15×10^{-4}						

Methanol CH_3OH		Carbon Dioxide CO_2		Acetone CH_3COCH_3		Diethyl Ether $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$		Normal Heptane $\text{CH}_3(\text{CH}_2)_5\text{CH}_3$	
Mass No.	amp/torr	Mass No.	amp/torr	Mass No.	amp/torr	Mass No.	amp/torr	Mass No.	amp/torr
1	1.53×10^{-5}	12	1.05×10^{-5}	1	1.05×10^{-5}	14	5.72×10^{-6}	14	6.00×10^{-6}
2	5.65×10^{-6}	18	9.66×10^{-5}	12	1.05×10^{-5}	15	5.40×10^{-6}	15	5.40×10^{-5}
12	1.02×10^{-5}	22	1.13×10^{-5}	13	3.16×10^{-5}	16	4.00×10^{-5}	26	3.84×10^{-5}
13	1.81×10^{-5}	28	7.48×10^{-5}	14	1.14×10^{-4}	15	1.40×10^{-4}	27	4.25×10^{-4}
14	3.50×10^{-5}	32	8.53×10^{-7}	15	5.58×10^{-4}	16	6.86×10^{-6}	28	9.6×10^{-5}
15	1.81×10^{-4}	44	2.98×10^{-4}	24	4.21×10^{-8}	19	2.52×10^{-5}	29	4.74×10^{-4}
16	6.78×10^{-6}	45	1.22×10^{-5}	25	2.53×10^{-5}	26	8.52×10^{-5}	30	1.32×10^{-5}
17	1.24×10^{-5}	46	5.81×10^{-6}	26	1.20×10^{-4}	27	3.50×10^{-4}	38	8.00×10^{-6}
18	1.24×10^{-5}	14	5.13×10^{-5}	27	1.52×10^{-4}	28	8.58×10^{-5}	40	4.56×10^{-5}
28	3.62×10^{-5}	15	5.13×10^{-6}	28	3.79×10^{-5}	29	6.48×10^{-4}	41	5.46×10^{-4}
29	3.28×10^{-4}	24	3.24×10^{-5}	29	7.37×10^{-5}	30	4.00×10^{-5}	42	3.00×10^{-3}
30	4.41×10^{-5}	25	8.94×10^{-5}	31	4.42×10^{-5}	31	1.05×10^{-3}	43	1.04×10^{-3}
31	5.12×10^{-4}	26	5.13×10^{-4}	32	3.28×10^{-4}	32	1.72×10^{-5}	50	9.60×10^{-6}
32	3.52×10^{-4}	27	5.42×10^{-4}	33	3.20×10^{-4}	33	5.72×10^{-8}	51	1.32×10^{-5}
33	9.04×10^{-5}	28	8.90×10^{-4}	34	8.13×10^{-4}	34	4.42×10^{-5}	53	2.4×10^{-5}
		29	2.03×10^{-5}	35	2.30×10^{-5}	35	1.39×10^{-4}	55	1.09×10^{-4}
				36	3.64×10^{-5}	36	5.40×10^{-4}	56	3.01×10^{-4}
				37	1.89×10^{-5}	37	1.89×10^{-4}	57	4.70×10^{-4}
				38	4.63×10^{-5}	38	3.95×10^{-4}	58	3.84×10^{-5}
				39	1.88×10^{-5}	39	1.26×10^{-5}	69	1.20×10^{-5}
				40	2.41×10^{-4}	40	1.26×10^{-5}	70	2.15×10^{-4}
				41	1.26×10^{-5}	41	2.63×10^{-4}	71	4.74×10^{-4}
				42	1.26×10^{-5}	42	2.63×10^{-4}	72	4.20×10^{-5}
				43	1.26×10^{-5}	43	2.63×10^{-4}	85	2.40×10^{-5}
				44	1.26×10^{-5}	44	1.26×10^{-5}	100	3.12×10^{-4}

TABLE I (Concluded)

O-Xylene $C_6H_4(CH_3)_2$		Benzene C_6H_6		Freon 113 CCl_2FCClF_2		Buxane $CH_3CH_2^2CH_3$		1,1-Dichloroethane CH_3CCl_2		1,1-Dichloroethylene CH_2ClCH_2Cl	
Mass No.	amp/torr	Mass No.	amp/torr	Mass No.	amp/torr	Mass No.	amp/torr	Mass No.	amp/torr	Mass No.	amp/torr
1	8.21×10^{-6}	1	6.71×10^{-6}	12	1.36×10^{-5}	1	3.41×10^{-6}	1	7.30×10^{-6}	1	1.0×10^{-5}
15	6.57×10^{-5}	15	1.34×10^{-5}	19	4.24×10^{-6}	14	5.68×10^{-6}	2	1.72×10^{-6}	12	5.91×10^{-6}
26	4.43×10^{-5}	25	9.40×10^{-6}	25	7.63×10^{-6}	15	4.32×10^{-5}	12	5.58×10^{-6}	13	1.04×10^{-5}
27	1.90×10^{-4}	26	4.83×10^{-5}	28	2.12×10^{-6}	27	3.22×10^{-4}	14	4.72×10^{-6}	14	1.82×10^{-5}
28	1.81×10^{-5}	27	4.43×10^{-6}	32	1.86×10^{-4}	26	9.49×10^{-5}	15	9.44×10^{-8}	15	6.36×10^{-6}
29	8.21×10^{-6}	28	8.05×10^{-6}	35	7.24×10^{-5}	29	3.81×10^{-4}	15	1.97×10^{-5}	24	8.18×10^{-6}
37	3.28×10^{-5}	29	5.37×10^{-6}	37	2.20×10^{-5}	24	1.24×10^{-5}	25	4.09×10^{-5}		
38	7.39×10^{-5}	36	1.34×10^{-5}	43	7.63×10^{-6}	30	1.25×10^{-5}	25	5.58×10^{-5}	26	1.65×10^{-4}
39	2.99×10^{-4}	37	6.44×10^{-5}	47	6.91×10^{-5}	37	6.25×10^{-6}	26	1.41×10^{-4}	27	5.36×10^{-4}
40	4.10×10^{-5}	37.5	5.37×10^{-5}	49	2.75×10^{-5}	38	2.16×10^{-5}	27	9.87×10^{-5}	28	4.50×10^{-5}
41	4.10×10^{-5}	38	8.19×10^{-5}	50	3.22×10^{-5}	39	1.76×10^{-4}	35	7.08×10^{-5}	29	3.64×10^{-5}
50	1.48×10^{-4}	39	1.66×10^{-4}	58	4.24×10^{-8}	40	4.03×10^{-5}	47	2.15×10^{-5}	38	4.09×10^{-6}
51	2.96×10^{-4}	41	1.21×10^{-5}	62	5.51×10^{-6}	50	7.95×10^{-6}	48	6.44×10^{-6}	43	5.00×10^{-6}
52	1.48×10^{-4}	42	6.71×10^{-6}	66	7.71×10^{-5}	51	1.19×10^{-5}	49	9.44×10^{-6}	47	1.73×10^{-5}
53	8.54×10^{-5}	43	1.07×10^{-5}	68	2.42×10^{-5}	52	4.54×10^{-6}	60	5.58×10^{-5}	48	2.95×10^{-5}
61	2.96×10^{-5}	48	6.71×10^{-6}	78	1.02×10^{-5}	53	1.82×10^{-5}	61	2.32×10^{-4}	49	1.69×10^{-4}
62	6.57×10^{-5}	49	4.16×10^{-5}	82	1.78×10^{-5}	54	1.08×10^{-5}	62	4.29×10^{-5}	50	2.09×10^{-5}
63	1.35×10^{-4}	50	2.01×10^{-4}	85	1.57×10^{-5}	55	6.82×10^{-5}	63	7.38×10^{-5}	51	5.04×10^{-5}
64	4.10×10^{-5}	51	2.32×10^{-4}	87	5.08×10^{-5}	56	3.90×10^{-4}	64	8.58×10^{-5}	59	4.54×10^{-5}
65	1.36×10^{-4}	52	1.99×10^{-4}	97	3.39×10^{-6}	57	6.82×10^{-4}	62	9.44×10^{-6}	60	1.95×10^{-5}
66	3.28×10^{-5}	53	1.74×10^{-5}	99	9.32×10^{-8}	58	3.98×10^{-5}	63	7.38×10^{-5}	61	6.45×10^{-5}
74	3.94×10^{-5}	55	8.05×10^{-6}	101	3.89×10^{-4}	55	6.82×10^{-5}	64	8.58×10^{-5}	63	8.77×10^{-5}
75	3.12×10^{-5}	56	9.40×10^{-6}	103	2.58×10^{-5}	56	3.90×10^{-4}	65	9.44×10^{-6}	64	1.27×10^{-4}
76	3.12×10^{-5}	57	5.37×10^{-6}	105	4.32×10^{-5}	57	6.82×10^{-4}	66	2.36×10^{-5}	65	2.36×10^{-4}
77	2.13×10^{-4}	51	1.07×10^{-5}	116	3.73×10^{-5}	58	3.98×10^{-5}	63	4.29×10^{-5}	61	5.00×10^{-6}
78	1.26×10^{-4}	62	1.07×10^{-5}	118	1.69×10^{-5}	65	2.27×10^{-6}	64	5.15×10^{-6}	62	3.87×10^{-5}
79	9.85×10^{-5}	83	4.03×10^{-5}	120	4.24×10^{-6}	67	3.98×10^{-6}	68	8.85×10^{-6}	63	8.77×10^{-5}
89	4.27×10^{-5}	73	1.61×10^{-5}	132	6.47×10^{-8}	68	3.98×10^{-6}	95	8.85×10^{-6}	64	1.27×10^{-4}
91	1.47×10^{-3}	74	4.70×10^{-5}	134	5.08×10^{-6}	69	1.70×10^{-5}	96	1.84×10^{-5}	65	5.00×10^{-6}
92	1.97×10^{-4}	75	2.15×10^{-5}	151	1.91×10^{-4}	70	1.02×10^{-5}	97	3.57×10^{-4}	97	5.00×10^{-6}
102	2.46×10^{-5}	76	3.89×10^{-5}	153	1.23×10^{-4}	71	3.58×10^{-5}	99	2.28×10^{-4}	98	7.09×10^{-5}
103	8.87×10^{-5}	77	1.65×10^{-4}	155	2.20×10^{-5}	84	1.82×10^{-4}	101	3.78×10^{-5}	100	4.54×10^{-5}
104	7.55×10^{-5}	78	1.14×10^{-3}	167	2.87×10^{-8}	86	1.82×10^{-5}	117	3.86×10^{-5}	102	8.18×10^{-6}
105	4.27×10^{-4}	79	6.71×10^{-5}	189	2.87×10^{-8}	87	1.82×10^{-5}	118	3.65×10^{-5}		
106	1.15×10^{-3}							121	1.12×10^{-5}		

Methylene Chloride CH_2Cl_2		Chloroform $CHCl_3$		Vinyl Chloride CH_2CHCl		Lithane CH_3CH_3	
Mass No.	amp/torr	Mass No.	amp/torr	Mass No.	amp/torr	Mass No.	amp/torr
1	1.20×10^{-5}	1	5.17×10^{-6}	1	1.49×10^{-5}	1	2.07×10^{-5}
12	1.83×10^{-5}	12	2.47×10^{-5}	2	1.33×10^{-5}	2	7.32×10^{-6}
13	3.52×10^{-5}	13	5.56×10^{-5}	13	2.25×10^{-5}	12	6.69×10^{-6}
14	4.58×10^{-5}	35	1.29×10^{-4}	14	1.94×10^{-5}	13	1.43×10^{-5}
35	9.01×10^{-5}	37	4.26×10^{-5}	15	5.45×10^{-7}	14	4.61×10^{-5}
36	1.97×10^{-5}	41.5	5.56×10^{-8}	24	2.39×10^{-5}	15	6.56×10^{-5}
37	3.03×10^{-5}	42.5	4.94×10^{-6}	25	8.98×10^{-5}	16	3.18×10^{-6}
41	2.48×10^{-5}	47	2.45×10^{-4}	26	2.37×10^{-4}	17	1.21×10^{-5}
42	1.62×10^{-5}	48	1.03×10^{-4}	27	7.11×10^{-4}	18	1.15×10^{-5}
43	5.63×10^{-6}	49	8.45×10^{-5}	33	3.96×10^{-5}	24	1.15×10^{-5}
47	1.10×10^{-4}	50	3.15×10^{-5}	37	1.55×10^{-5}	25	6.05×10^{-5}
48	6.06×10^{-5}	70	6.17×10^{-6}	47	2.37×10^{-5}	26	3.34×10^{-4}
49	5.88×10^{-4}	72	3.71×10^{-5}	48	1.21×10^{-5}	27	4.83×10^{-4}
50	3.24×10^{-5}	83	5.82×10^{-4}	49	9.10×10^{-5}	28	1.54×10^{-3}
51	1.76×10^{-4}	85	3.65×10^{-4}	59	9.95×10^{-8}	29	3.25×10^{-4}
82	5.63×10^{-6}	87	5.80×10^{-5}	60	2.85×10^{-3}	30	4.52×10^{-4}
83	1.41×10^{-5}	117	6.17×10^{-6}	61	5.16×10^{-5}	31	1.08×10^{-5}
84	3.20×10^{-4}	118	2.16×10^{-5}	62	4.50×10^{-1}	103	2.91×10^{-4}
86	2.02×10^{-4}	120	1.98×10^{-5}	64	1.44×10^{-5}	105	4.90×10^{-5}
88	3.38×10^{-5}	122	6.17×10^{-6}	65	4.74×10^{-6}	117	9.90×10^{-6}

Freon 11 CCl_3F		Lithane CH_3CH_3		Freon 11 CCl_3F		Lithane CH_3CH_3	
Mass No.	amp torr	Mass No.	amp torr	Mass No.	amp torr	Mass No.	amp torr
12	2.60×10^{-5}	31	7.92×10^{-5}	32	5.21×10^{-6}	13	1.13×10^{-5}
35		35	1.22×10^{-4}	36	2.80×10^{-5}	20	5.15×10^{-6}
37		37	4.06×10^{-5}	38	5.73×10^{-6}	24	3.30×10^{-5}
38		38		47	7.50×10^{-5}	25	1.20×10^{-4}
47		47		49	4.50×10^{-5}	26	2.06×10^{-4}
49		50	1.04×10^{-5}	56	8.75×10^{-5}	37	2.58×10^{-5}
56		66	2.76×10^{-5}	68	4.69×10^{-6}	47	4.33×10^{-5}
68		70	4.69×10^{-6}	72	3.12×10^{-6}	48	1.96×10^{-5}
72		72	7.32×10^{-6}	82	2.03×10^{-5}	50	8.25×10^{-6}
82		84	1.35×10^{-5}	85	3.64×10^{-6}	58	2.58×10^{-5}
85		101	4.52×10^{-4}	101	4.52×10^{-4}	59	1.37×10^{-4}
101		103	2.91×10^{-4}	103	2.91×10^{-4}	60	8.67×10^{-5}
103		105	4.90×10^{-5}	105	4.90×10^{-5}	61	7.73×10^{-5}
105		117	9.90×10^{-6}	117	9.90×10^{-6}	62	2.12×10^{-4}
117		118	8.83×10^{-6}	118	8.83×10^{-6}	95	2.99×10^{-4}
118		120	1.08×10^{-5}	120	2.00×10^{-6}	98	1.88×10^{-4}
120		122	4.74×10^{-6}	122		100	2.89×10^{-5}

TABLE II
STANDARD PARTIAL PRESSURE VALUES AND PARTIAL PRESSURE SOLUTIONS

Type of Gas	Partial Pressure Standards (torr)	Solutions by Matrix Inversion				Solutions By Iteration	
		First Set		Second Set			
		(torr)	% Error	(torr)	% Error	(torr)	% Error
Nitrogen	$1.02 \cdot 10^{-6}$	$1.09 \cdot 10^{-6}$	+ 6.9	$8.38 \cdot 10^{-7}$	-17.8	$1.06 \cdot 10^{-6}$	+ 3.9
Oxygen	$9.95 \cdot 10^{-7}$	$9.86 \cdot 10^{-6}$	- 0.9	$9.86 \cdot 10^{-7}$	- 0.9	$9.86 \cdot 10^{-7}$	- 0.9
Argon	$1.01 \cdot 10^{-6}$	$1.20 \cdot 10^{-6}$	+18.8	$1.20 \cdot 10^{-6}$	+18.8	$1.19 \cdot 10^{-6}$	+17.8
Carbon Dioxide	$1.00 \cdot 10^{-6}$	$1.12 \cdot 10^{-6}$	+12.0	$1.12 \cdot 10^{-6}$	+12.0	$1.11 \cdot 10^{-6}$	+11.0
Hydrogen	$1.58 \cdot 10^{-7}$	$1.57 \cdot 10^{-7}$	- 0.6	$1.57 \cdot 10^{-7}$	- 0.6	$1.57 \cdot 10^{-7}$	- 0.6
Methane	$1.74 \cdot 10^{-7}$	$1.67 \cdot 10^{-7}$	- 3.5	$1.62 \cdot 10^{-7}$	- 6.9	$1.69 \cdot 10^{-7}$	- 2.9
Carbon Monoxide	$1.74 \cdot 10^{-7}$	$5.92 \cdot 10^{-8}$	-66.0	$2.77 \cdot 10^{-7}$	+59.2	$2.84 \cdot 10^{-7}$	+63.2
Ethane	$1.73 \cdot 10^{-7}$	$1.81 \cdot 10^{-7}$	+ 4.6	$1.81 \cdot 10^{-7}$	+ 4.6	$1.79 \cdot 10^{-7}$	+ 3.5
Butane	$9.12 \cdot 10^{-8}$	$8.93 \cdot 10^{-8}$	- 2.1	$8.95 \cdot 10^{-8}$	- 1.9	$9.54 \cdot 10^{-8}$	+ 4.6
Propene	$9.19 \cdot 10^{-8}$	$7.86 \cdot 10^{-8}$	-14.5	$7.86 \cdot 10^{-8}$	-14.5	$9.29 \cdot 10^{-8}$	+ 1.1
Ethylene	$9.29 \cdot 10^{-8}$	$1.18 \cdot 10^{-7}$	+27.0	$1.09 \cdot 10^{-7}$	+17.4	$1.03 \cdot 10^{-7}$	+10.9
Propane	$9.72 \cdot 10^{-8}$	$8.25 \cdot 10^{-8}$	-15.1	$8.20 \cdot 10^{-8}$	-15.6	$1.00 \cdot 10^{-7}$	+ 2.9

TABLE III
EXPERIMENTAL SPECTRUM OF WORKING STANDARD, 12-COMPONENT MIXTURE

ℓ (Mass No.)	H_ℓ (amp)	ℓ (Mass No.)	H_ℓ (amp)
1	$1.36 \cdot 10^{-11}$	37	$1.73 \cdot 10^{-11}$
2	$7.72 \cdot 10^{-11}$	38	$3.13 \cdot 10^{-11}$
12	$6.92 \cdot 10^{-11}$	39	$1.03 \cdot 10^{-10}$
13	$2.10 \cdot 10^{-11}$	40	$1.11 \cdot 10^{-9}$
14	$1.12 \cdot 10^{-10}$	41	$1.37 \cdot 10^{-10}$
15	$1.59 \cdot 10^{-10}$	42	$9.22 \cdot 10^{-11}$
16	$3.64 \cdot 10^{-10}$	43	$1.50 \cdot 10^{-10}$
19	$3.3 \cdot 10^{-12}$	44	$1.17 \cdot 10^{-9}$
19.5	$3.0 \cdot 10^{-12}$	45	$1.44 \cdot 10^{-11}$
20	$1.00 \cdot 10^{-10}$	46	$4.5 \cdot 10^{-12}$
22	$1.37 \cdot 10^{-11}$	49	
24	$6.3 \cdot 10^{-12}$	50	$1.5 \cdot 10^{-12}$
25	$2.57 \cdot 10^{-11}$	51	$1.7 \cdot 10^{-12}$
26	$1.46 \cdot 10^{-10}$	52	
27	$2.65 \cdot 10^{-10}$	53	$1.2 \cdot 10^{-12}$
28	$1.65 \cdot 10^{-9}$	54	
29	$2.22 \cdot 10^{-10}$	55	$2.1 \cdot 10^{-12}$
30	$8.57 \cdot 10^{-11}$	56	$1.4 \cdot 10^{-12}$
31	$2.3 \cdot 10^{-12}$	57	$5.2 \cdot 10^{-12}$
32	$7.70 \cdot 10^{-10}$	58	$2.81 \cdot 10^{-11}$
36	$7.0 \cdot 10^{-12}$	59	$1.3 \cdot 10^{-12}$

Note: Current peaks $< 1.0 \cdot 10^{-12}$ were not measured.

TABLE IV
 $\cos^2\theta_{ij}$ VALUES INDICATING
 ILL-CONDITIONING

i (Mass No.)	j (Mass No.)	$\cos^2\theta_{ij}$
12	44	0.43
14	16	0.59
15	16	0.95
25	26	0.98
25	27	0.63
25	28	0.44
26	27	0.73
26	28	0.50
27	28	0.49
27	29	0.52
27	38	0.31
27	39	0.32
28	30	0.42
29	43	0.40
37	38	0.99
37	39	0.98
37	40	0.93
37	41	0.92
37	42	0.93
38	39	0.99
38	41	0.93
38	42	0.92
39	41	0.96
39	42	0.95
41	42	0.98
43	58	0.94

TABLE V
 ILL-CONDITIONING OF INITIAL
 SYSTEM

i (Mass No.)	j (Mass No.)	$\cos^2\theta_{ij}$
14	16	0.59
27	28	0.49
27	29	0.52
28	30	0.42
29	43	0.40

TABLE VI
 ILL-CONDITIONING OF FINAL
 SYSTEM

i (Mass No.)	j (Mass No.)	$\cos^2\theta_{ij}$
12	44	0.43
25	28	0.44
28	30	0.42
29	43	0.40

TABLE VII
ERROR SPECTRUM CALCULATION, TENTH ITERATION

ℓ (Mass No.)	Experimental H_ℓ (amp)	Error Spectrum (amp)	Error Spectrum (Percent)
2.0	7.720(-11)	4.632(-16)	6.001(-04)
12.0	6.919(-11)	4.906(-17)	7.090(-05)
14.0	1.119(-10)	4.119(-15)	3.677(-03)
15.0	1.590(-10)	5.826(-15)	3.664(-03)
16.0	3.639(-10)	-5.758(-12)	-1.582(00)
25.0	2.569(-11)	1.731(-15)	6.739(-03)
26.0	1.459(-10)	5.855(-13)	4.010(-01)
27.0	2.650(-10)	-8.867(-12)	-3.346(00)
28.0	1.650(-09)	-2.224(-10)	-1.348(01)
29.0	2.219(-10)	-2.708(-11)	-1.220(01)
30.0	8.570(-11)	1.790(-15)	2.089(-03)
32.0	7.700(-10)	7.235(-17)	9.396(-06)
37.0	1.729(-11)	-2.869(-12)	-1.659(01)
38.0	3.130(-11)	3.831(-14)	1.224(-01)
39.0	1.029(-10)	-1.141(-11)	-1.108(01)
40.0	1.109(-09)	1.010(-14)	9.107(-04)
41.0	1.369(-10)	-2.145(-11)	-1.566(01)
42.0	9.219(-11)	-7.597(-12)	-8.241(00)
43.0	1.499(-10)	-1.478(-11)	-9.857(00)
44.0	1.170(-09)	-3.008(-14)	-2.571(-03)
58.0	2.809(-11)	4.420(-13)	1.573(00)

Note: (x) denotes a factor of 10^x .

TABLE VIII
COMPARISON OF EXPERIMENTAL AND CALCULATED SPECTRA

ℓ (Mass No.)	Calculated H_ℓ (amp)	Experimental H_ℓ (amp)	% Difference of Experimental H_ℓ
2	$7.78 \cdot 10^{-11}$	$7.72 \cdot 10^{-11}$	- 0.8
12	$5.95 \cdot 10^{-11}$	$6.92 \cdot 10^{-11}$	+16.3
14	$1.08 \cdot 10^{-10}$	$1.12 \cdot 10^{-10}$	+ 3.7
16	$3.62 \cdot 10^{-10}$	$3.64 \cdot 10^{-10}$	+ 0.5
27	$2.61 \cdot 10^{-10}$	$2.65 \cdot 10^{-10}$	+ 1.5
28	$1.68 \cdot 10^{-9}$	$1.65 \cdot 10^{-9}$	- 1.8
29	$2.39 \cdot 10^{-10}$	$2.22 \cdot 10^{-10}$	- 7.1
30	$8.26 \cdot 10^{-11}$	$8.57 \cdot 10^{-11}$	+ 3.7
32	$7.77 \cdot 10^{-10}$	$7.70 \cdot 10^{-10}$	- 0.9
40	$9.42 \cdot 10^{-10}$	$1.11 \cdot 10^{-9}$	+18.0
41	$1.55 \cdot 10^{-10}$	$1.37 \cdot 10^{-10}$	-11.6
43	$1.58 \cdot 10^{-10}$	$1.50 \cdot 10^{-10}$	- 5.1
44	$1.05 \cdot 10^{-9}$	$1.17 \cdot 10^{-9}$	+11.4
58	$2.64 \cdot 10^{-11}$	$2.81 \cdot 10^{-11}$	+ 6.4

TABLE IX
NORMALIZED CRACKING PATTERNS FROM TWO INDEPENDENT CALIBRATIONS OF THE BENDIX 17-210V

Mass No.	Methane CH ₄		Carbon Monoxide CO		Nitrogen N ₂		Ethylene CH ₂ :CH ₂		Ethane CH ₃ :CH ₃		Oxygen O ₂		Argon Ar		Propene CH ₂ :CHCH ₃		Propane CH ₃ CH ₂ CH ₃		Carbon Dioxide CO ₂		Mass No.		
	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2			
1	1.50	1.05					2.20	1.22	1.34	0.78						1.77	1.12	1.08	0.66			1	
2	0.89	0.28					0.34	0.26	0.48	0.75						0.45	0.36	0.31	0.24			2	
12	1.67	1.92	3.56	3.61			1.47	1.42	0.43	0.39						0.75	0.77	0.24	0.25	4.65	4.68	12	
13	5.80	6.40					2.98	2.76	0.93	0.94						1.39	1.34	0.72	0.60			13	
14	12.7	13.2	0.43	0.42	6.92	6.94	5.76	5.53	2.99	2.99						3.41	3.18	2.29	2.31			14	
15	73.8	76.5					0.58	0.57	4.26	3.91	0.21	0.11	11.0	11.0			5.18	4.86	6.93	7.10			15
16	100	100	1.72	1.92												0.18	0.30	0.24	0.24	9.72	9.57	16	
17	1.13	1.34																				17	
19																2.30	2.15	0.94	0.98			19	
19.5																1.42	1.42	0.58	0.51			19.5	
20																9.25	9.27	1.69	1.78	1.04	0.97	20	
20.5																0.55	0.49	0.27	0.24			20.5	
22																				1.13	1.14	22	
24																						24	
25																						25	
25																						25	
27																						27	
28			100	100	100	100	60.9	60.0	31.4	33.3						32.4	33.9	42.2	42.7			28	
29			1.10	1.38	0.81	0.88	100	100	100	100	1.14	1.44				2.65	0.44	63.6	64.0	7.51	7.92	29	
30			0.42				2.28	2.92	21.1	22.1	29.4	31.0						100	100	-	0.13	30	
31																						31	
32																						32	
36																						36	
37																						37	
38																						38	
39																						39	
40																						40	
41																						41	
42																	72.4	73.2	6.35	9.34			42
43																	2.88	2.96	28.8	28.6			43
44																			42.2	42.4	100	100	44
45																			1.35	1.57	1.22	1.42	45
46																			0.59	0.51			46

TABLE X
ERRORS INTRODUCED BY 2-PERCENT ERROR IN H₂₉

Gas	Assumed Solution (torr)	Δp by Matrix Inversion		Solutions by Iteration	
		(torr)	% Error	(torr)	% Error
Carbon Monoxide	4·10 ⁻⁶	-9.87·10 ⁻¹⁰	-0.02	3.997·10 ⁻⁶	-0.08
Hydrogen	1·10 ⁻⁶	-3.31·10 ⁻¹¹	-0.00	9.999·10 ⁻⁷	-0.01
Propane	5·10 ⁻⁷	+1.39·10 ⁻⁸	+2.78	5.015·10 ⁻⁷	+0.30
Methane	4·10 ⁻⁷	+6.84·10 ⁻¹⁰	+0.17	3.998·10 ⁻⁷	-0.05
Ethylene	3·10 ⁻⁷	-8.50·10 ⁻⁹	-2.83	2.999·10 ⁻⁷	-0.03
Nitrogen	2·10 ⁻⁷	+1.49·10 ⁻⁹	+0.75	2.005·10 ⁻⁷	+0.25
Ethane	1·10 ⁻⁷	-8.46·10 ⁻¹⁰	-0.85	9.989·10 ⁻⁸	-0.11
Propene	8·10 ⁻⁸	-9.65·10 ⁻¹⁰	-1.21	7.960·10 ⁻⁸	-0.50
Butane	4·10 ⁻⁸	-3.63·10 ⁻⁹	-9.07	3.992·10 ⁻⁸	-0.20
Oxygen	4·10 ⁻⁸	+1.55·10 ⁻¹¹	+0.04	4.167·10 ⁻⁸	+4.2
Argon	3·10 ⁻⁸	-2.02·10 ⁻¹⁰	-0.67	3.009·10 ⁻⁸	+0.30
Carbon Dioxide	2·10 ⁻⁸	-6.84·10 ⁻⁹	-34.20	1.854·10 ⁻⁸	-7.3

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13 ABSTRACT Procedures are discussed for using mass spectrometers to make absolute partial pressure measurements of complicated residual gas mixtures in high vacuum systems. The details of the matrix inversion technique and an iteration procedure for calculating partial pressures from mass spectrometer data are presented. Performance of a Bendix Model 17-210V time-of-flight mass spectrometer and calibration data obtained are given. These data indicate that short-term instrument stability cannot be assumed for mass spectrometers which use electron multipliers for ion detection, and that instrument linearity can be assumed only under certain operating conditions. The data show that frequent, in-place, mass spectrometer calibrations are necessary. The matrix inversion technique and the iteration procedure were evaluated experimentally by reducing the 17-210V spectrum of a 12-component mixture of common residual gases whose partial pressures were known. The experimental results indicate that the iteration technique is the simplest to apply, and that it produces more accurate partial pressure solutions. It is concluded that accuracies of ± 15 percent in partial pressure measurements are obtainable.		

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